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- (71) Applicant (*for all designated States except US*): ADSIL LC [US/US]; 1 Hargrove Grade, Suite 1-K, Palm Coast, FL 32137 (US).
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- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): SCHUTT, John, B. [US/US]; 2403 Peachstone Court, Silver Spring, MD 20905 (US).
- (74) Agent: HAINES, Robert, L.; Sherman & Shalloway, 413 N. Washington Street, Alexandria, VA 22314 (US).
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(54) Title: SELF-CLEANING SURFACES USING POLYSILOXANE COATING COMPOSITION WITH PHOTOCATALYTIC PROPERTY

(57) Abstract: Food stains, beverage stains, oil and gasoline stains and other organic based stains on various building and paving materials, such as concrete, cement, and other masonry materials, are caused to spontaneously disappear as a result of photocatalytically induced oxidation, upon exposure to artificial or natural UV light, wherein titanium oxy groups, bonded within the Amorphous Ti-O is the photocatalyst. The substrate is coated with a self-cleaning silane based coating composition in which amorphous Ti-O is chemically bonded in the polysiloxane backbone. The self-cleaning coating also provides durable, corrosion resistant coatings on non-metal surfaces. A typical composition may include one or a mixture of silanes, such as methyltrimethoxysilane and phenyltrimethoxysilane. The coating compositions may be formulated with either acidic or basic catalysts. Concrete, sidewalks treated with the self-cleaning silane coating compositions do not require high-pressure water washing to remove food, beverage, oil or gasoline stains.

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SELF-CLEANING SURFACES USING POLYSILOXANE
COATING COMPOSITIONS WITH PHOTOCATALYTIC PROPERTY
CROSS-REFERENCE TO RELATED APPLICATIONS

- This application is a continuation-in-part of copending application, Serial No. 5 09/778,921, filed February 8, 2001, which, in turn, claims priority from Provisional Applications SN 60/185,354 and SN 60/185,367, both filed February 28, 2000, and from Provisional Application 60/236,158, filed September 29, 2000.

BACKGROUND OF THE INVENTION

Field of the Invention

- 10 The present invention relates to metallic and non-metallic surfaces which are rendered self-cleaning. More particularly, this invention relates to the use of certain polysiloxane coating compositions for protecting surfaces, such as cement, concrete and brick walkways and building structures, from forming permanent stains when exposed to organic substances, such as foods, beverages, gasoline spills, oil spills, and the like. Even more particularly, this 15 invention relates to photocatalytically active silane-based, coating compositions of the type disclosed in my prior copending application, SN 09/778,921, the disclosure of which is incorporated herein, in its entirety, by reference thereto, particularly, namely, those compositions containing compounds of titanium alcoholates incorporated into the coating layer.

20 Discussion of the Prior Art

- In my recently issued U.S. Patent 5,929,129, there are described corrosion resistant coatings provided by aqueous-alcoholic dispersions of the partial condensate of monomethyl silanol (obtained by hydrolysis of monomethyl alkoxysilane) alone or in admixture with 25 minor amounts of other silanol, e.g., gamma-glycidyloxy silanol, wherein the reaction is catalyzed by divalent metal ions, e.g., Ca^{+2} , typically from alkaline earth metal oxides. When these coating are applied to, e.g., boat hulls, such as aluminum hulls, they are highly effective in preventing corrosion from salt water for extended periods.

- In my provisional application SN 60/185,367, filed February 28, 2000, I described non-aqueous coating compositions containing, for example, (A) silanes represented by 30 formula (1):

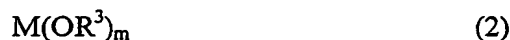


where R¹ is a lower alkyl group, phenyl group, 3,3,3-trifluoropropyl group, γ -glycidylxypropyl, γ -methacryloxypropyl group, N-(2-aminoethyl)-3-aminopropyl group or aminopropyl group,

R² is a lower alkyl group; and

5 n is a number of 1 or 2;

(B) vinyltriacetoxysilane and/or colloidal aluminum hydroxide and/or at least one metal alcoholate of formula (2):



where M is a metal of valence m, R³ is a lower alkyl group; and m is a number of 2 to 4. In
10 other embodiments, the compositions may further include one or more of (C) ethylorthosilicate, ethylpolysilicate or colloidal silica dispersed in lower alkanol; (D) boric acid, optionally dissolved in lower alkanol; (E) γ -glycidylxypropyltrimethoxysilane; (F) finely divided solid lubricant.

In addition to the immediately above described compositions, there is described in my
15 aforementioned copending application SN 09/778,921, corrosion resistant coatings which do not require acidic pH's to catalyze the polymerization of silanols to form polysiloxane coatings and which may be applied to steel or other acid degradable surfaces. Application of certain of the coating compositions disclosed in this application were noted to be useful for coating concrete substrates.

20 While protection of concrete and other non-metallic masonry and building materials and metal surfaces against attack by acid, for example, was generally contemplated for the inventor's prior compositions, there is still a need to provide protection of a wide range of surfaces from staining caused by organic pigments, including, for example, beverages, e.g., soft drinks, and alcoholic beverages, foodstuffs, e.g., ketchup, mustard, ice cream, blood and
25 blood products, gasoline, oils, and many other substances which may inadvertently be spilled or deposited on walkways, walls, floors, equipment and other structures in manufacturing and food and beverage processing facilities and the like. Staining is often particularly acute in high traffic areas, such as in and near amusement parks, sports and entertainment stadium, railroad stations, downtown city streets, and the like. Currently, the only effective means of
30 removing such stains is often by hosing with high-pressure water sprays. However, not only is this expensive but, the use of high-pressure water, will significantly accelerate the

degradation of the concrete, cement, brick, etc., substrate.

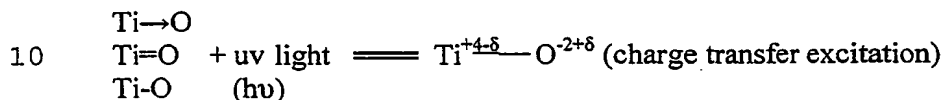
On the other hand, it has been proposed to use titanium dioxide (TiO_2) coatings to provide a photocatalytically-activated self-cleaning (referred to as "PASC") surface on various substrates, including a range of architectural materials and glass. Typically, methods for applying a PASC coating to a substrate involve, forming a layer of TiO_2 particles, for example, by a sol-gel method. The more recent prior art in this technology has often focused on the improvement in the adherence of the titanium dioxide to the substrate, including the use of various adhesives. Representative of the patent art in this area, mention may be made of, U.S. 5,595,813 and its division, U.S. 5,643,436, to Takatoshi Ogawa, et al, titled, "ARCHITECTURAL MATERIAL USING METAL OXIDE EXHIBITING PHOTOCATALYTIC ACTIVITY"; U.S. 5,811,192 to K. Takahama, et al; U.S. 6,013,372 to M. Hayakawa, et al; U.S. 6,027,766 to C.B. Greenberg, et al; U.S. 6,027,797 to T. Watanabe, et al; U.S. 6,054,227 to C. B. Greenberg, et al; U.S. 6,090,489 to M. Hayakawa, et al; U.S. 6,139,803 to T. Watanabe, et al; U.S. 6,154,311 to F. L. Simmons, Jr., et al; U.S. 6,165,256 to M. Hayakawa, et al; U.S. 6,159,421 (T. Fujii); U.S. 6,268,050B1 (T. Watanabe, et al); and U.S. 6,277,346B1 (S. Murasawa, et al).

As will be apparent from review of the prior disclosures of articles and methods utilizing photocatalytically active catalysts, the photocatalytically active catalysts, generally semiconductor metal oxides, including especially titanium oxides, are present in the crystalline form, preferably the rutile or anatase form. This is true, regardless of the starting material, which in some cases, is a TiO_2 precursor, for example, titanyl sulfate, titanium alkoxides, and the like, and whether the form of titanium oxide, is TiO_2 , or hydrated titanium oxide, hydrous titanium oxide, metatitanate, orthotitanate, or titanium hydroxide (see, e.g., column 4, of U.S. 6,277,346B1). In addition, the photoconductive catalyst layers generally include high concentrations of the titanium oxide photocatalyst particles, even if the layer itself is very thin.

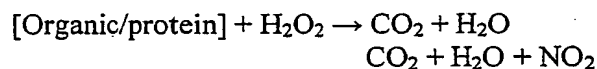
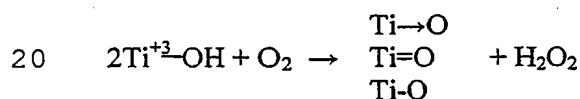
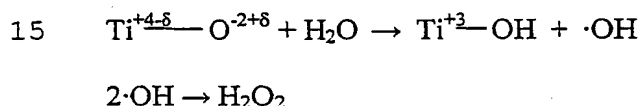
It has now surprisingly been found that the coating compositions of my prior application, SN 09/778,921, which contain a titanium compound, in which titanium oxide is present in copolymerized form, chemically integrated into a polymer backbone, are effective in as self-cleaning coatings, wherein the titanium oxide is still able to function effectively as a photocatalyst, in the presence of ultraviolet (UV) light. In particular, it has been discovered,

in the course of investigating the benefits of the coating compositions as general protective coatings for concrete, that stains caused by organic substances, spontaneously (i.e., without further intervention) disappeared within several hours to only one or more days. Further investigation of this phenomenon suggested that the cause of this phenomenon was the

- 5 oxidative conversion of the organic residues, e.g., protein residues, presumed to occur by the formation of hydrogen peroxide, wherein the hydrogen peroxide, in turn, was formed from ambient moisture, under the catalytic influence of photocatalyzed titanium, as shown by the following reaction mechanisms:



(where $\text{Ti} \rightarrow \text{O}$, $\text{Ti}=\text{O}$ and $\text{Ti}-\text{O}$, represent the alternative bonding arrangements of Ti and O)



- 25 The presented invention was completed on the basis of this discovery. Accordingly, it is an object of the invention to provide a method for coating porous, non-metallic architectural and construction materials, such as concrete, whereby the coated concrete is self-cleaning, e.g., resistant to the formation of permanent stains caused by contact with
- 30 organic substances.

The foregoing and other objects of this invention are described in further detail below.

SUMMARY OF THE INVENTION

Accordingly, this invention provides a method for protecting porous and non-porous, metallic and non-metallic, materials against staining by organic substances.

35

In one aspect, this invention provides a method for providing a protective and self-cleaning coating on concrete and masonry surfaces, such as concrete and brick walkways,

external concrete, brick and cinder block building structures, and other such materials which are subject to exposure to natural (e.g., sunlight) or artificial (e.g., fluorescent) UV irradiation.

In another aspect, the self-cleaning protective coatings of this invention are applied in the interior spaces of buildings, such as, for example, manufacturing and processing plants and facilities, hospitals, apartment building and family dwellings, and the like, including, for example, floors and walls, as well as to any structures and/or appliances, therein and especially those surfaces expected or likely to come into contact with organic debris, e.g., food and/or beverages, blood products, and the like, such as, equipment, food handling surfaces, and the like

The protective and self-cleaning coating compositions applied to the surface to be protected in the method of the present invention include silane coating compositions having Ti-O groups bonded in the siloxane matrix.

In accordance with one embodiment hereof, the protective coating composition is formed by admixing the at least one silane of formula (1) [component (A)], a titanium alcoholate of formula (2) [component (B)], silane condensation catalyst, which is, preferably, one or both of (i) acid compound [component (C)] and/or (ii) basic compound [component (D)], and water [component (E)].

Thus, in one embodiment of the invention, the protective coating composition is formed by admixing and applying to the substrate

(A) at least one silane of the formula (1)



wherein

R^1 is a lower alkyl group, a phenyl group or a functional group, including at least one of vinyl, acrylic, amino, mercapto, or vinyl chloride functional group; and

R^2 is a lower alkyl group;

(B) titanium alcoholate;

(C) silane condensation catalyst, which comprises base component and/or boric acid and/or aluminum isopropoxide; and

(D) water.

In a particularly preferred embodiment, the protective coating is formed from an

aqueous coating composition containing mixed valence silane condensation catalysts.

According to this embodiment of the invention, an aqueous coating composition is formed by admixing (A) at least one silane of formula (1) given above; (B) titanium alcoholate, especially of formula $Ti(OR^3)_4$, where R^3 represent a lower alkyl group, (C) (i) trivalent boric acid or derivative thereof, (ii) aluminum isopropoxide and/or (iii) at least one divalent metal silanol condensation catalyst compound, preferably, an hydroxide and/or carbonate of a divalent metal, such as calcium or magnesium hydroxide or carbonate; and (D) water; and, optionally, one or more of (E) ethyl polysiloxane; and (H) lower alkanol solvent.

The invention also provides the novel coated articles obtained by coating the surface as described herein.

The present invention, including specific applications thereof, will now be described in further detail by way of specific embodiments and examples, although the invention is not limited to these specific embodiments.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

The present invention provides a method for providing self cleaning surfaces, including, for example, architectural and structural materials, such as, concrete and similar materials, including, in particular, walkways, building exteriors, work surfaces, concrete tanks and storage vessels, and similar structures from other masonry materials, including, for example, brick, mortar, concrete, cement, blocks, limestone, stone, and other generally hard, porous, architectural building and construction materials; and metal and plastic materials, including, for example, manufacturing equipment and appliances. Since the self-cleaning property is achieved upon exposure to ultraviolet (UV) irradiation, it is preferred that the surfaces to be protected are outdoor surfaces, such as walkways, e.g., streets, roads, pathways, pavement, sidewalks, etc., and outside (external) building structures, e.g., walls of building, window casings, bridge abutments, above ground concrete or metal tanks and other storage structures, and the like. However, effective self-cleaning also takes place under irradiation with artificial UV light, e.g., from indoor or outside mercury or fluorescent lighting fixtures, generally, any light source providing light having a wavelength of about 400 microns or lower. Accordingly, both indoor and outdoor surfaces may be protected by the method of the present invention.

As used herein, the term "self-cleaning," means that although stains may not be

prevented from forming on the substrates treated according to the present invention, any such stains, especially those based on organic matter, e.g., carbohydrates, such as sugars, proteins, starches, and the like, will be "spontaneously" removed, that is, by exposure to sunlight or artificial UV irradiation, or combination of sunlight and artificial lighting. However, it should be understood that the process of self-cleaning under irradiation by UV light is a photocatalytic oxidation reaction, as described above, and may require several to many hours, up to, for example, up to 1 or more days, e.g., about 1,2 or 3 days, for essentially complete stain removal, depending on, for example, severity and nature of the stain, the particular coating, including the amount of the Ti-O groups, the intensity and duration of UV exposure, and the like.

The stains which may be effectively prevented/removed, according to the present invention include, for example, organic based stains, such as, for example, proteins, carbohydrates, e.g., sugars, starches, oils, gasoline and other organic substances, i.e., compounds containing carbon and hydrogen as the major and essential elements, often with nitrogen and/or oxygen. Thus, stains caused by proteinaceous or starchy food products, or sugar based food and condiment products, including often difficult or hard to remove materials, such as ketchup, mustard, mayonnaise, blood, and the like; beverages, such as, for example, soft drinks, alcoholic beverages, juices, and the like. Oily and gasoline spills are another major source of staining on, especially, roadways and walkways, especially near or in the vicinity of grassy areas or construction sites, as well as on the floors, walls and equipment, of manufacturing plants, warehouses, etc. where machinery oils and fuels are subject to leaking and spilling. All of these types of stains may be effectively prevented from permanently staining substrates treated with the silane based Ti-O coating compositions of the present invention.

In this regard, it is believed that while alkoxides of other transition metal oxides, e.g., zirconium and hafnium, may also function in a similar manner to the titanium alkoxides, the oxides of Zr and Hf, require even shorter wavelength irradiation, e.g., blue, light, such as light of wavelength of about 300 microns or lower, therefore, would not be as effective or efficient under most circumstances as the preferred coatings based on Ti-O incorporated into the siloxane coating matrix, as titanium alkoxides.

In the self-cleaning and protective coatings used in the present invention, it is believed

by the inventor, that the effectiveness and efficiency of the photocatalytically induced oxidation reaction, results, at least in part, by the chemical incorporation of the Ti→O groups in the polysiloxane matrix of the cured coatings, such as, for example, is believed to be the case where the Ti→O groups are derived from titanium alcoholate. The incorporation of the

5 Ti→O groups in the polysiloxane matrix is, furthermore, believed to include chemical bonding of the Ti atom to two adjacent silanol groups, as in a titanyl structure, such that, the vacant valencies of Ti^{+4} are filled as either TiO or $Ti(OH)_2$. This construction allows electrons to hop relatively freely between the surface interfacial layer and the environment whereby the ambient moisture (H_2O) is converted to hydrogen peroxide oxidizing agent. In

10 contrast, as seen from the disclosures of the above noted prior patents relating to photocatalytic coatings, the photocatalytic phenomenon is one of electron-hole transport, again, dependent on the present of crystalline titanium oxides.

However, it is also within the scope of the invention to incorporate titania, e.g., pigment or UV absorber, into the silane coating compositions. In this case, although the TiO_2

15 particles will not be incorporated into the matrix of the coating, the silane of the coating will attach to the titania particles and may, therefore, facilitate the absorption of UV light and, therefore, promote the photocatalytic activation of the Ti→O in the polysiloxane matrix.

As examples of silanes of formula (1), wherein R^1 is an alkyl group or aryl group, mention may be made of, for example, methyltrimethoxysilane, ethyltrimethoxysilane,

20 ethyltriethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, isopropyltrimethoxy silane, n-butyltrimethoxy silane, isobutyltrimethoxy silane, phenyltrimethoxy silane, preferably methyltrimethoxy silane. In the case where R^1 is a functional group, mention may be made, for example, of N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, 3-

mercaptopropyltrimethoxy silane, 3-mercaptopropyltriethoxy silane, 3-aminopropyltriethoxy

25 silane, 3-(meth)acryloxypropyl trimethoxy silane, 3-(meth)acryloxypropyltriethoxy silane, n-phenylaminopropyltrimethoxy silane, vinyltriethoxy silane, vinyltrimethoxy silane, allyltrimethoxy silane, and any of the aminosilane catalysts, described hereinbelow as component (A-1).

As used herein, the expression "functional group" is intended to include any group,

30 other than hydroxyl, (including alkoxy, aryloxy, etc.), which is hydrolyzable to provide, *in situ*, a reactive group (e.g., reactive hydrogen) which will react, in other than a condensation

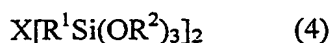
reaction, with the substrate (e.g., metal), itself, or other reactive components in or from the coating composition.

The functional groups, in addition to the hydroxyl group (by hydrolysis of the (OR²) groups), tend to form three-dimensional or cross-linked structure, as well known in the art.

5 Moreover, in the various embodiments of the invention, it is often preferred to use mixtures of two or more silane compounds of formula (1). Mixtures of at least phenyltrimethoxysilane and methyltrimethoxysilane are often especially preferred.

Generally, total amounts of silane compounds of formula (1) will fall within the range of from about 40 to about 90 percent by weight, preferably from about 50 to about 85 percent
10 by weight, based on the total weight of silanes, acid component and water.

In addition to silane compound(s) of formula (1), the composition may additionally include a bis-trifunctional aminosilane, such as represented by the following formula (4):



where R¹ and R² are as defined above, and X represents an amino group (-NH) or keto group

15 $\begin{array}{c} O \\ || \\ (C<) \end{array}$, as a basic catalyst, not requiring acid stabilization. As a representative example of aminosilane or ketosilane catalyst according to formula (4), mention may be made of, for example, bis(trimethoxypropylsilane) amine, bis(trimethoxyethylsilane) amine,
20 di(trimethoxybutylsilane) ketone, di(trimethoxypropylsilane) ketone, and the like. The silane compounds of formula (4) function as a less active basic catalyst, not requiring acidic passivation and, when used, are usually from about 1 to about 10 parts, preferably, from about 2 to about 8 parts, of compound of formula (4) per 100 parts of silane compound(s) of formula (1).

25 The coating compositions contain, as well known in the field of siloxane and silicone coatings, a silanol condensation catalyst (C), which may be a base component, for example, an inorganic base, such as, for example, calcium hydroxide, aluminum hydroxide or zinc hydroxide, or mixture thereof; or an organic base component, such as, for example, aminosilane.

30 When present, the amount of the base component is generally, up to about 2%, such as, for example, from about 0.1 to 2.0%, by weight of the composition, especially, from about 0.2 to 1.6%.

The use of an acid as the silanol condensation catalyst (C) is not preferred in the present invention because acids tend to quench the reaction, therefore, conventionally known acid condensation catalysts, such as, lower alkanolic acids or ortho-phosphorous acid (H_3PO_3), are not preferably used. However, it has been found that boric acid may be used as an acidic silanol condensation catalyst component may be advantageously used as condensation catalyst in the present invention. The boric acid, when used, may be added as free acid or as inorganic salt thereof, such as zinc borate, alkaline earth metal (e.g., calcium) borate, or ammonium borate, or organic derivative, e.g., boron methoxide.

Generally, total amounts of the boric acid component will fall within the range of from about 0.3 to about 4 percent by weight, preferably from about 0.5 to about 3%, preferably, from about 0.5 to about 2.5 percent by weight, based on the total weight of silanes, acid component and water.

Another preferred silanol condensation catalyst, which may be used by itself, or in combination with either or both of the basic catalyst and boric acid component, is aluminum isopropoxide.

Generally, the amounts of aluminum isopropoxide, when present, may be the same as the amounts specified above for the boric acid component. When both boric acid component and aluminum isopropoxide are present, the total amounts will generally fall within the ranges noted above, namely, between about 0.3 to about 4 percent by weight, preferably, from about 0.5 to about 3% by weight, such as, from about 0.5 to 2.5 percent by weight, based on the total weight of silanes and condensation catalyst(s) and water.

Since the coating compositions of this invention are most effective at neutral or slightly basic pH's, it is often preferred, especially when boric acid, or other acidic groups are included in the composition, to incorporate a basic aminosilane condensation catalyst, generally in an amount to maintain a pH in the range of from about 6.8 to about 8.0, preferably, from about 7.0 to 7.9.

As examples of the basic aminosilane catalyst (A-1), mention may be made of, for example, aminoethyl-triethoxysilane, beta-amino-ethyltrimethoxysilane, beta-aminoethyl-triethoxysilane, beta-amino-ethyl-tributoxysilane, beta-aminoethyltripropoxysilane, alpha-aminoethyl-trimethoxysilane,

- alpha-aminoethyl-triethoxysilane, gamma-aminopropyltrimethoxysilane,
gamma-aminopropyl-triethoxysilane, gamma-aminopropyl-tributoxysilane,
gamma-amino-propyltripropoxysilane, beta-aminopropyl-trimethoxysilane,
beta-aminopropyl-triethoxysilane, beta-amino-propyltripropoxysilane,
5 beta-aminopropyl-tributoxysilane, alpha-aminopropyl-trimethoxysilane,
alpha-aminopropyltriethoxysilane, alpha-aminopropyl-tributoxysilane,
alpha-aminopropyl-tripropoxysilane, N-aminomethylaminoethyl-trimethoxysilane,
N-aminomethylaminomethyl-tripropoxysilane,
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N-(gamma-aminopropyl)-beta-aminoethyl-triethoxysilane, N-(gamma-aminopropyl)-beta-aminoethyl-tripropoxysilane, N-methyl aminopropyl trimethoxysilane, beta-aminopropyl methyl diethoxysilane, gamma-diethylene triaminepropyltriethoxysilane, and the like.

- 5 Of these, 3-(2-aminoethylamino)propyltrimethoxy silane [also known as N-(2-aminoethyl)-3-aminopropyltrimethoxysilane], and 3-aminopropyltrimethoxy silane, are especially preferred.

Aminosilanes of formula (4), above, may also be used.

- 10 The total amount of water will usually fall within the range of from about 10 to about 60 percent by weight, preferably from about 10 to about 45 percent by weight, based on the total weight of silanes, acid component and water.

Some or all of the water may be provided by other components, e.g., aqueous solution of boric acid (about 5% by weight of H_3BO_3).

- 15 Since the presence of metallic and other impurities may have an adverse effect on the properties of the resulting coatings, preferably, the water is distilled or de-ionized water.

- 20 While general and preferred ranges of amount for the film-forming and catalytic components have been described above, it will be recognized by those skilled in the art, that these amounts may be increased or decreased as necessity demands and that the optimum amounts for any particular end use application may be determined by the desired performance. In this regard, for example, when the amount of catalyst is reduced, the time to achieve freedom from tack will increase. Similarly, when the amount of the catalyst(s) is (are) increased, this may lead to increased rates of cracking, loss of adhesion and performance loss of the resulting coating.

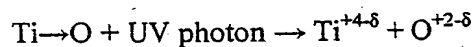
- 25 In accordance with the present invention, the coating to be applied to the concrete, etc., substrate, includes a titanium oxy group, e.g., $Ti \rightarrow O$ group, (where the " \rightarrow " bond connotes bonding occurring because the Ti has donated two electrons to the same oxygen atom); or $Ti-O$ (where the " $-$ " bond connotes an oxygen obtaining its electrons from neighboring cations), derived from a titanium alcoholate, which also functions as a polymerization catalyst for the silanol condensation reaction and, therefore, assists in film formation (this is the function envisioned for the metal alcoholates in the copending
- 30

application SN 09/778,921). Preferred metal alcoholates are those of the formula $Ti(OR^3)$, where R^3 is a lower alkyl group, e.g., C_1 - C_6 straight or branched chain alkyl group, preferably C_2 - C_4 alkyl group, most preferably, isopropyl, isobutyl or n-butyl.

Although not wishing to be bound to any particular theory of operation, based on current knowledge, it is believed that the mechanism for removal of interfacial organic contaminants from a coating interface comprised of a siloxy network copolymerized with titanium oxy molecules by their cooperatively photogenerated hydroxy free radicals and hydrogen peroxide. Since both titanium and silicon have vacant d- and p-orbitals, respectively, they can share the temporary caging of charge.

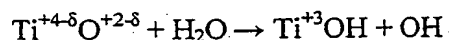
As described generally by the equations given above, the excitation process driving the photocatalysis involves UV excited transfer of an electron from oxygen into a titanium oxy electron transfer orbital for momentary storage in the vacant d-orbital structure on titanium, or the creation of an electron hole pair, when a molecular matrix is present in which, a band structure at some level may be postulated.

This process may be represented, for example, as follows:



where $Ti \rightarrow O$ represents, for example, $Ti-O-Ti$ or $Ti-O-Si$, in the amorphous siloxy matrix.

In the presence of atmospheric moisture, then, there can occur



followed by: $2OH \rightarrow H_2O_2$,

followed by (in the presence of molecular oxygen): $2Ti^{+3}OH + O_2 \rightarrow H_2O_2$ or $2OH$.

Only minor amounts of titanium alkoxide are required to function as photocatalysts effective to provide self-cleaning property to substrates coated thereby. In addition to the self-cleaning property, the coating compositions of this invention tend to be water repellant. However, because the Ti^{4+} incorporated in the coated films have empty d-orbitals, trace water molecules tend to be attracted to the surface, such that water vapor and oxygen molecules may penetrate into the surface layer. Amounts of titanium alkoxide (as TiO_2) as low as about 0.25%, by weight, of the coating, preferably, from about 0.5 to 2%, more preferably, from about 0.6 to about 1.4%, especially, from about 0.7 to about 1.2%, by weight, should be effective to provide the desired photocatalytic activity. Within this range, substantially all of

the titanium oxy groups are copolymerized in the polysiloxane matrix and effectively distributed throughout the coated film. Still further, at these low levels, none or substantially none of the Ti is bonded to the substrate. An amount of titanium alkoxide to provide a ratio of 1 TiO₂ molecule per from about 42 to about 83 silanol molecules provides effective self-cleaning property.

The compositions of this embodiment may further include one or more additional additives for functional and/or esthetics effects, such as, for example, silicates, organic solvents and co-solvents, UV absorbers, metal catalysts and the like.

The above-noted optional ingredients may be used singly or in any combination in the coating composition of this invention, so long as the self-cleaning property is still present.

As examples of silicate component, mention may be made of ethyl or methyl orthosilicate or ethyl polysilicate. These silicates may be hydrolyzed, for example, from about 28% to about 52% silica. Especially preferred in this regard is tetraethylsilicate (TEOS) which has been subjected to controlled hydrolysis, providing a mixture of TEOS and, from about 20% to about 60% polydiethoxysilane oligomers. For example, a 50% hydrolysis product may be referred to herein as "polydiethoxysilane (50%)."

Generally, total amounts of silicate component, when used, will fall within the range of from 0 to about 45 percent by weight, preferably from 0 to about 25 percent by weight, based on the total weight of silanes, acid component and water.

As examples of mono-lower alkyl ether of alkylene (e.g., ethylene) glycol, mention may be made of mono-C₁-C₆-alkyl ethers of ethylene glycol, such as, for example, monomethyl ether, monoethyl ether, monopropyl ether, monobutylether, monopentylether or monohexylether, preferably monoethyl ether of ethylene glycol.

Generally, total amounts of the mono-lower alkyl ether of ethylene glycol, when used, will fall within the range of from 0 to about 15 percent by weight, preferably from 0 to about 6 percent by weight, based on the total weight of silanes, boric acid and water.

As an example of ultra-violet light absorber, mention may be made of titanium dioxide in finely powdered form, e.g., having an average particle diameter of about 20 nm. Other inorganic or organic ultra-violet light absorbers may be utilized in so far as they do not

interfere with the objects of this invention.

Generally, total amounts of the ultra-violet light absorber, when used, will fall within the range of from 0 to about 10 percent by weight, preferably from 0 to about 5 percent by weight, more preferably not more than about 1 percent by weight, based on the total weight
5 of silanes, silanol condensation catalyst component(s) and water.

As examples of organic solvents, mention may be made of lower alkanol, e.g., C₂-C₄ alkanols, preferably isopropanol. Other organic solvents, such as, for example, acetone, methyl ethyl ketone, ethyl acetate, and the like may also be used.

Generally, total amounts of organic solvent, such as, lower alkanol, will fall within a
10 range of from 0 to about 50 percent by weight, preferably from 0 to about 30 percent by weight, based on the total weight of silane(s), acid component and/or base component, titanium alkoxide and water. In some cases, however, substantially higher amounts may be convenient, especially where, for example, the coating compositions are applied by spraying as an aerosol or mist.

15 As examples of the metal catalysts, other than the titanium alkoxides, mention may be made of, for example, colloidal aluminum hydroxide (e.g., from aluminum isopropoxide), and other metal alkoxides, such as, for example, hafnium alkoxides and zirconium alkoxides.

Within the above general proportions, the silane component (A) may be used in an amount of from about 15 to about 25 parts by weight, preferably as a mixture of from about
20 15 to about 20 parts by weight of methyltrimethoxysilane and from about 1 to about 5 parts by weight of phenyltrimethoxysilane; the titanium alkoxide (B) is present in the range of from about 0.05 to 1 part by weight, preferably, from about 0.1 to 0.8 part by weight, such as about 0.25 or 0.30 part by weight, the base component (C)(i), when present, is used in an amount of from about 0.1 to 3 weight percent, preferably from about 0.2 to 2.5 weight
25 percent; the boric acid component (C)(ii) and/or aluminum isopropoxide (C)(iii), when present, is or are used in an amount of from about 0.2 to about 0.8 part by weight; provided that at least one of (C)(i) or (C)(ii) or (C)(iii), will generally always be used; water (D) is used in an amount of from about 2.5 parts by weight to about 22 parts by weight; the silicate component is used in an amount of from 0 to about 15 parts by weight; the mono-lower alkyl
30 ether of ethylene glycol is used in an amount of from 0 to about 3 parts by weight; the ultra-violet light absorber is used in an amount of from 0 to about 2 parts by weight; and lower

alkanol is used in an amount of from 0 to about 20 parts by weight.

The present coating composition may be formed by mixing the above-noted components and allowing them to react. A suitable reaction time is typically from about 30 minutes to about 12 hours, more usually, from about 60 minutes to about 2 hours. If no lower
5 alkanol is present, frequent shaking may be necessary to achieve a shorter reaction time.

For ease of handling, the coating composition may be provided as a two or three container system, e.g., the silane component and any silicate component, if present, being provided in a first container and all other components being provided in a second or second and third container. The water may be provided separately from the other components. The
10 contents of the two or three containers may be mixed shortly prior to use and allowed to react for an appropriate reaction time, as noted above.

It is often preferred to use a multivalent catalyst system to polymerize the organosilane of formula (1). For example, the mixed multivalent catalyst may include a divalent metal compound, such as hydroxide or carbonate of calcium, magnesium or other
15 alkaline earth metal; a trivalent metal compound, such as, for example, boric acid or other compound of boron or aluminum; and the titanium alkoxide, as a tetravalent metal catalyst.

According to this embodiment, the proportions of the respective catalysts may be selected based on the desired properties but generally in terms of metal ions, weight ratios of $M^{+2}:M^{+3}:M^{+4}$ of from about 0.1-1:0.05-1:0.1-2, preferably from about 0.4-1:0.2-1:0.5-1,
20 provide good results. The multivalent catalyst system may be used with any of the coating compositions described herein.

As described above, the self-cleaning and protective coating compositions of this invention may be applied to a wide range of metallic and non-metallic surfaces. For
example, mention may be made of generally porous architectural building and construction
25 materials, such as cement, concrete, limestone and other stone materials, as well as, e.g., siliceous, ceramic, vitreous substrates. The coating compositions may also be applied to plastic substrates, for example, and not by way of limitation, , e.g., polyolefins, polyesters, polyamides, polyimides, polycarbonates, polyetherimides, polysulfones, and the like, glass, alkali metal silicates, and the like. The coatings also adhere well to and may be used to coat
30 metal surfaces, e.g., steel, stainless steel, aluminum, and the like. Also, any of the substrates may be painted or, otherwise, colored or pigmented, without adversely affecting adherence of

the coating to the paint coating.

The application of the self-cleaning and protective coating to sidewalks, walkways, concrete, or cement paths, etc., in high-traffic environments, often associated with a high degree of spillage of potentially staining food and beverage products, as well as gasoline, oils and other organic and hydrocarbon fluids, offers obvious benefits. By providing the self-cleaning coatings, the necessity to use high pressure water, or other potentially damaging cleaning treatment, can be completely avoided, thereby greatly extending the useful life of the walkway, etc., structure.

The self-cleaning and protective coating compositions of this invention when applied to a substrate, such as those mentioned herein, will readily penetrate even narrow and microscopic crevices or pores of the substrate, to form strong adherent bonds with the substrate. Although not wishing to be bound by any particular theory of operation, it is believed that the penetration and adherent bond formation is achieved, in part, because of the absence of large organic molecules from the invention coating systems.

The coating compositions contemplated herein may be formulated as solventless, aqueous or non-aqueous systems (although, in most cases, at least a catalytic amount of water is eventually added, directly or taken from the atmosphere). For example, the solventless systems may contain a mixture of methyltrimethoxysilane and phenyltrimethoxysilane and, catalyst, such as, for instance, tetrabutoxytitanate.

The self-cleaning coating composition may be applied in conventional manner, preferably by dipping, wiping, brushing or spraying, however, especially when applied to outside pre-existing structures, e.g., sidewalks, building exteriors and the like, it is apparent that brushing or spraying, most preferably spraying, will be used.

Only thin coatings, on the order of about 2000 nm, or less, will provide self-cleaning and protective (e.g., corrosion resistance) properties. Generally, the coating compositions of the present invention are effective when applied to a coating (film) thickness (after cure) in the range of from about 5 to about 150 millionths of an inch, however, if desired to provide even superior corrosion protection, thicker films, up to about several mil, e.g., up to about 5/1000 inch (5 mil), preferably, up to about 2 mil, may be applied.

Moreover, multiple applications of the coating composition may be applied to achieve thicker coatings, including, particularly, covering any pinholes which may exist when only

a single coating application is used. In this regard, it is generally understood in the art that a polysiloxane coating will not accept (e.g., adhere) another polysiloxane coating layer.

Accordingly, it is a distinct advantage of the coatings of the present invention that multiple layers may be provided and this is an important and useful feature of the present invention.

- 5 In addition to covering pinholes or otherwise forming thicker and longer lasting coatings, the ability of the coatings of this invention to accept multiple layers provides the additional advantage that, even if photocatalytic activity diminishes with time, it is a simple matter to reapply the coating composition without any special treatment of the substrate, although, it is usually preferred to remove loose dirt or other loose residues before re-coating the substrate.
- 10 Naturally, however, for best results, the old surface should be cleaned, usually with an aqueous surfactant solution, then rinsed and dried, before applying additional or new layer of the subject coating composition.

- The ability to accept multiple coatings is especially observed when boric acid or derivative and aluminum isopropoxide are used jointly as catalysts in the invention coating
- 15 compositions with the titanium alkoxide.

The following examples are illustrative and are not intended to limit the invention in any way. Unless stated otherwise, all parts and percentages are by weight. In the following examples the water used is distilled or deionized water.

EXAMPLE 1

- 20 To methyltrimethoxysilane (20 parts), aluminum isopropoxide (0.2 parts or 0.3 parts) is added, with stirring. Stirring is continued for about 1 hour or until the mixture becomes uniformly cloudy. Then, water (3.8 parts) is added and mixing is continued for about 1 additional hour, until the mixture, when applied to a coupon, will tackify. Then there is
-
- added titanium tetrabutoxide (0.8 parts) and stirring is continued for an additional 30 minutes.

- 25 The so-formed liquid mixture may be applied by wiping, foam brushing, conventional brushing or spraying to concrete, cement, limestone, and other architectural, building or construction material substrates and will dry to a tack-free condition in about 60 minutes or less.

- 30 After the coating becomes tack-free, it may be overcoated with additional liquid mixture to build-up the final thickness. The resulting coating becomes insensitive to

isopropyl alcohol and impervious to gasoline, in less than four hours.

Similar results are obtained when the amount of water is increased to about 6 parts and the amount of titanium tetrabutoxide is increased to 1.2 parts. In the event that precipitation of the titanium compound is observed, the mixture may be filtered to remove the precipitate.

EXAMPLE 2

To 15 parts methyltrimethoxysilane, there is added, while stirring, 5 parts propyltrimethoxysilane or 5 parts phenyltrimethoxysilane. To this mixture, 0.3 parts boric acid is added followed by addition of 0.2 to 0.3 parts tetrabutoxytitanate.

The mixture is allowed to clear. Then, 10 to 13 parts of water is added slowly to avoid excessive heat build-up. The resulting composition may be applied to a substrate while it is still warm or after further heating by reaction. Alternatively, the composition may be stored and applied after as long as about 6 days after water addition. Application may be by spraying, wiping, brushing, etc.

As another example of an organic-solvent free self-cleaning coating composition, a mixture of 15 parts methyltrimethoxysilane and 5 parts phenyltrimethoxysilane is combined with 0.2 to 0.35 parts of tetrabutoxytitanate. While stirring, 2.4 parts water is added. After about 15 minutes the resulting composition is ready to be applied to cement or other substrate.

20

This composition may also be advantageously applied for the protection of interior and exterior building materials from, for example, deposition and growth of mildew or infectious organisms, especially in salt air environments, such as coastlines, industrial areas and the like. For instance, the composition may be used to coat ceramic roofing tiles, concrete, galvanized steel, duct works (e.g., interior surfaces), etc.

EXAMPLE 3

5 parts of phenyltrimethoxysilane are added to a container containing 15 parts methyltrimethoxysilane. While mixing, 0.3 part of tetrabutoxy titanate are added, along with 2 parts of polydiethylsiloxane (approx. 50%), and 15 parts of isopropyl alcohol. After mixing, 10 parts of an aqueous 3% boric acid solution are added and, after waiting eight hours, the resulting coating composition may be applied, by brushing or spraying. The cured

compositions will be corrosion resistant and self-cleaning.

In this example, similar results will be obtained when, instead of 0.3 part of tetrabutoxy titanate, 0.2, 0.4, 0.5 or 0.6 part of tetrabutoxy titanate are used.

EXAMPLE 4

5 10 parts of a 3% boric acid solution are placed in a first container. 20 parts of methyltrimethoxysilane, 10 parts of isopropyl alcohol and 0.5 part of tetrabutoxy titanate are mixed in a second container. The contents of the two containers can then be mixed together and allowed to react to form a self-cleaning coating composition.

By eliminating isopropyl alcohol, the rate of emulsification can be increased by
10 increasing batch size.

EXAMPLE 5

A silane-alcohol mixture (Pot A) is prepared by mixing 15 parts of methyltrimethoxy-
silane, 5 parts of isobutyltrimethoxysilane and 1.1 parts of polydiethylsiloxane (~50%) to
form a homogeneous silane-alcohol solution. Separately, there is prepared a mixture (Pot B)
15 obtained by combining 11.3 parts of a 3% solution of boron methoxide in isopropyl alcohol,
2 parts of polydiethoxysiloxane (~50% solids), 0.4 parts of tetrabutoxytitanate, and 2 parts of
methyl-trimethoxysilane. The mixture in Pot B is allowed to react for 24 hours and is then
added to the silane-alcohol solution in Pot A. The resulting mixture may be sprayed on
concrete walkways.

20 EXAMPLE 6

20 parts of methyltrimethoxysilane and 20 parts isopropyl alcohol are mixed and the
resulting mixture is combined with 0.25 parts of titanium tetraisopropoxide under stirring
until the titanium tetraisopropoxide is partially dissolved. To this mixture 6 parts water is
added. After stirring for about one hour, the mixture is ready for applying to the intended
25 substrate, by brushing, spraying, etc. To extend pot life, phenyltrimethoxysilane may be
introduced to the coating composition.

EXAMPLE 7

140 parts methyltrimethoxysilane and 140 parts isopropyl alcohol are mixed and
catalyzed using 1.0 part of titanium tetraisopropoxide. The resulting mixture is stirred until
30 the catalyst is dissolved, after which 42 parts of water are added. The reaction is complete
when the mixture is nearly at room temperature. The reaction mixture is applied, by spraying

or brushing, onto a concrete, asphalt, or cement walkways or other surfaces.

EXAMPLE 8

To a mixture formed by combining 20 parts methyltrimethoxysilane, 20 parts isopropyl alcohol, and 2 parts polydiethoxysiloxane (~52% solids), there is added a catalyst
5 containing 0.6 parts boron methoxide and 0.2 parts titanium tetraisopropoxide. After the solids are dissolved, water (6 parts) is added to complete the catalysis. The resulting mixture is allowed to stand (react) for about 1 hour. The reaction product may be applied to architectural building or construction materials to wet thicknesses of 0.5 mil or 1 mil, respectively, and allowed to cure under ambient conditions for about 7 days. In this example,
10 the titanate and boron ethoxide each function to hydrolyze ethyl silicate. These compositions have good stability and, consequently, a very long pot life.

EXAMPLE 9

This example shows a two part mixed valence catalyst system for silane catalyzation. In particular, tetrabutoxy titanate (Ti+4) functions as the primary catalyst, and boric acid
15 (B+3) as secondary catalyst. Together, these two catalysts are believed to enter the ethyl polysilicate into the final matrix and thereby create a photocatalyzable self-cleaning silicone coating.

This composition, even without addition of a stabilizer, has a pot life of about 2 days.

20 Twenty (20) parts methyltrimethoxysilane, 5 parts phenyltrimethoxysilane and 20 parts isopropyl alcohol are combined and thoroughly mixed. To this mixture is first added 0.2 parts of boric acid followed by addition of 4 parts of polydiethoxysiloxane (50%). After the boric acid is dissolved, 0.6 parts tetrabutoxy titanate and then 6.5 parts water are added. By adding the water slowly, premature hydrolysis of the tetrabutoxy titanate may be
25 prevented.

As a test of effectiveness as a self-cleaning coating, the following procedure is carried out.

The resulting composition is sprayed onto a cement slab which is located outdoors in Palm Coast, Florida. A non-diet cola drink is poured on the treated concrete and on a non-
30 treated concrete slab. In both cases, after drying, the treated and non-treated concrete slabs are left with dark stains from the soft drink. Both slabs are left outdoors, with equal daytime

exposure to the sunlight and, after 2 days, the stain completely disappears from the treated slab but no change is observed in the non-treated slab.

Similar results to the above are obtained using a three part mixed valence catalyst. In this case, after about one hour following the addition of water, 1.6 parts of a 0.5% solution-
5 suspension of calcium hydroxide in isopropyl alcohol is added and the mixture is allowed to react for at least one hour. Calcium hydroxide (Ca^{+2}) functions here, as tertiary catalyst.

Similar results to the above are also obtained by replacing the boric acid with an equal amount of aluminum isopropoxide (0.2 parts) as the secondary catalyst. Also, similarly good results are obtained by using a mixture of 0.2 parts boric acid and 0.2 parts aluminum
10 isopropoxide.

EXAMPLE 10

The following composition is prepared.

Twenty parts of methyltrimethoxysilane are combined with 5 part of phenyltrimethoxysilane in a container to which is added 4 parts of a polydiethylsiloxane
15 hydrolyzed to about 50% solids. To this mixture is added 0.3 parts boric acid. The mixture is stirred until the boric acid is dissolved. Next, 0.5 parts of tetrabutoxytitanate are added, while stirring is continued. Finally, 6.7 parts of water are slowly added to avoid a color change. After the catalyzed reaction proceeds for about two hours, the mixture may be applied, by spraying, on the substrate to be protected. The coating will cure under ambient
20 conditions in about one week. The resulting coating can withstand immersion in HCl bath for a minimum of two hours.

WHAT IS CLAIMED IS:

1. A method for treating a substrate to render the substrate self-cleaning upon exposure to ultraviolet irradiation, said method comprising, forming on the substrate a polysiloxane coating having titanium oxy groups from titanium alkoxide, bonded in the polysiloxane backbone, whereby, organic based stains formed on the coated substrate and exposed to UV light, will spontaneously disappear.
2. The method according to claim 1, wherein said substrate comprises a walkway.
3. The method according to claim 1, wherein said substrate comprises the external surface of a building structure
4. The method according to claim 1, wherein the substrate is metallic.
5. The method according to claim 1, wherein the substrate is plastic.
6. The method according to claim 1, wherein the substrate is a painted surface.
7. The method according to claim 1, wherein the titanium oxy groups are derived from titanium tetraisopropoxide.
8. The method according to claim 1, wherein the titanium oxy groups are derived from titanium tetrabutoxide.
9. The method according to claim 1, which further comprises overcoating the polysiloxane coating with at least one additional layer of said polysiloxane coating.
10. The method according to claim 1, wherein the siloxane coating is formed by depositing on the substrate an aqueous coating composition formed by admixing
 - (A) at least one silane of the formula (1)

$$R^1Si(OR^2)_3 \quad (1)$$

 wherein
 - R¹ is a lower alkyl group, a phenyl group or a functional group containing at least one of vinyl, acrylic, amino, mercapto, or vinyl chloride functional group; and
 - R² is a lower alkyl group;
 - (B) titanium alcoholate of the formula Ti(OR³)₄ wherein R³ is a lower alkyl group;
 - (C) silane condensation catalyst; and,
 - (D) water.
11. The method of claim 10, wherein the silane condensation catalyst (C) comprises boric acid or derivative thereof.

12. The method according to claim 10, wherein the silane condensation catalyst (C) comprises aluminum isopropoxide.

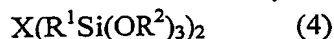
13. The method according to claim 10, wherein the silane condensation catalyst (C) comprises a mixture of boric acid or derivative thereof and aluminum isopropoxide.

5 14. The method according to claim 13, which further comprises overcoating the polysiloxane coating with at least one additional layer of said polysiloxane coating.

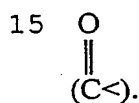
15. The method according to claim 10, wherein the titanium alcoholate is titanium tetraisopropoxide or titanium tetrabutoxide.

16. The method according to claim 10, wherein the silane of formula (1) comprises a
10 mixture of methyltrimethoxysilane and phenyltrimethoxysilane.

17. The method according to claim 10, wherein said coating composition further comprises a silane compound of formula (4):



where R^1 and R^2 are as defined above, and X represents an amino group (-NH) or keto group



18. The method according to claim 10, wherein the aqueous coating composition further comprises (F) lower alkanol.

20 19. The method according to claim 10, wherein in formula (1) R^2 is methyl and R^1 is lower alkyl.

20. The method according to claim 10, wherein said silane of formula (1) comprises a mixture comprising methyltrimethoxysilane and phenyltrimethoxysilane.

21. The method according to claim 10, wherein said siloxane coating further
25 comprises (I) ultra-violet light absorber.

22. The method according to claim 10, wherein the titanium alcoholate comprises titanium tetraisopropoxide or titanium tetrabutoxide.

23. The method according to claim 1, wherein the siloxane coating is formed by applying to the substrate an aqueous coating composition formed by admixing

30 (A) at least one silane of the formula (1)



wherein

R^1 is a lower alkyl group, a phenyl group or a functional group including at least one of vinyl, acrylic, amino, mercapto, or vinyl chloride functional group; and

R^2 is a lower alkyl group;

(B) a titanium alcoholate of formula $Ti(OR^3)_4$ wherein R^3 represents a lower alkyl
5 group;

(C) silane condensation catalyst comprising a mixture of (i) at least one divalent metal hydroxide and/or carbonate and (ii) at least one trivalent metal compound catalyst; and

(D) water.

24. The method according to claim 23, wherein the trivalent metal compound catalyst
10 (C) comprises at least one of boric acid, boric acid derivative, and aluminum isopropoxide.

25. A coated substrate produced by the method of claim 1.

26. A coated concrete substrate produced by the method of claim 1.

27. The coated concrete substrate according to claim 26, which is a walkway.

28. A coated metal substrate produced by the method of claim 1.

15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/28570

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B05D 3/06, 7/00

US CL : 427/407.1, 419.5, 553

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,753,827 A (YOLDAS et al) 28 June 1988 (28.06.1988), abstract, column 2, line 10	1-6, 8, 9, 25-28
---	- column 3, line 68, column 5, lines 43 - 55, claims.	7, 10-24
Y		
X	US 6,072,018 A (WILKES et al) 06 June 2000 (06.06.2000), entire document, especially	1-10, 15, 18, 21, 22,
---	abstract, column 4, lines 25 - 26, column 5, lines 10-35, column 7, lines 10-20.	25-28
Y		7, 10-24
Y	US 5,623,030 A (TSUMURA et al) 22 April 1997 (22.04.1997), column 9, line 6.	11, 13, 14, 23, 24
Y	US 4,552,941 A (KEOGH, M.J.) 12 November 1985 (12.11.1985), column 3, line 65.	12, 13, 14, 23, 24
X	WO 01/64804 A1 (SHUTT, J.B.) 07 September 2001 (07.09.2001), entire document.	1-28
---		16, 17, 20
Y		
X	US 6,037,289 A (CHOPIN et al) 14 March 2000 (14.03.2000), entire document,	1-9
	especially column 8, line 45 - column 9, line 21.	

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

02 November 2002 (02.11.2002)

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703)305-3230

Date of mailing of the international search report

27 NOV 2002

Authorized officer

Shrive P. Beck

Telephone No. (703) 308-0661

Jean Proctor
Paralegal

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INTERNATIONAL SEARCH REPORT

PCT/US02/28570

Continuation of B. FIELDS SEARCHED Item 1:

427/407.1, 419.5, 553, 558, 402, 409, 419.2; 106/287.14, 287.16, 287.24, 287.26; 528/10, 12, 13, 16, 17, 18, 20, 25, 29, 222, 485

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